



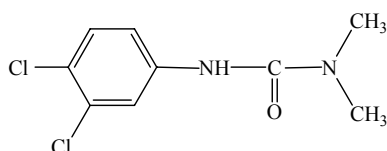
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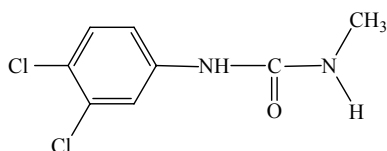
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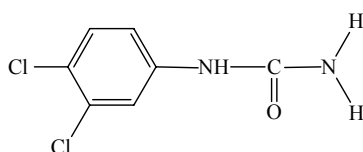
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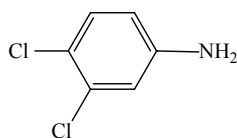
Diuron
N'-(3,4-dichlorophenyl)-*N,N*-dimethylurea



DCPMU
N'-(3,4-dichlorophenyl)-*N*-methylurea



DCPU
N'-(3,4-dichlorophenyl)-*N*-methylurea



DCA
3,4-dichloroaniline

BRITISH GEOLOGICAL SURVEY

INTERNAL REPORT IR/03/029

The fate of diuron and its metabolites in calcareous sediments – second annual report

D C Goody, D Allen, S Hannay, I Harrison and D J Lapworth

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Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB

☎ 01491-838800 Fax 01491-692345

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU

☎ 01793-411500 Fax 01793-411501
www.nerc.ac.uk

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Summary

An experimental plot has been established since January 2001 on a calcareous soil in southern England to investigate the fate and transport of diuron (*N*'-[3,4-dichlorophenyl]-*N,N*-dimethylurea), a commonly used phenylurea herbicide. In late January 2002 an agricultural grade of diuron was applied to the existing plot and to an adjacent plot on to the soil surface at a rate of 6.7 kg/ha along with a potassium bromide conservative tracer applied at 200 kg/ha. Hand augured samples were taken at regular intervals over the next 125 days with samples collected down to 54 cm. Porewaters were extracted from the soil cores by using high speed centrifugation and the supernatant fluids were retained for analysis by HPLC for diuron and three of its metabolites, *N*'-[3,4-dichlorophenyl]-*N,N*-methylurea (DCPMU), *N*'-3,4-dichlorophenylurea (DCPU) and 3,4-dichloroaniline (DCA). The centrifuged soil was retained and then extracted the solid phase material with methanol prior to HPLC analysis for the same suite of analytes.

Variability within the same plot between different sample periods and between plots makes understanding and quantifying the system difficult. The generally more moist Plot B contains higher concentrations of diuron and metabolites in the porewaters than Plot A whereas Plot A contains generally higher concentrations in the solid phase than Plot B.

In year 2, the rate of degradation over a 50 day period is faster in both plots than it was in Plot A in year 1. After 120 days metabolites account for more than 50% of total pesticide found in solid phase in both plots. In the liquid phase metabolites account for 33% in Plot A and 51% in Plot B. The rate of degradation is faster in Plot B than Plot A for both solid phase and porewaters. In all cases, the dominant metabolite is DCPMU. The highest percentage of DCA occurs in solid phase and porewaters of Plot A which might suggest some enhanced degradation of DCPU or could be a residual from the 2001 application. During the study period roughly 100% of residues were accounted for.

Metabolites are more strongly retained in the solid phase than the parent compounds as demonstrated by the generally higher K_d values. From highest to lowest K_d DCA>DCPMU>DCPU>Diuron. Although greater rates of degradation are associated with the solid phase, this also suggests that metabolites can remain as a potential source of groundwater contamination long after the parent compound has disappeared from both porewaters and solid phase.

1 Introduction

Contamination of groundwater by pesticides has brought increased environmental concern over the past decade (Foster et al., 1991; Soutter and Pannatier 1996; Chilton et al., 2000; Foster 2000; Gaus 2000). In the United States, a considerable body of work exists relating to the occurrence of both parent compound pesticides and their metabolites in aquifers (Thurman et al., 1992; Baker et al., 1993; Lawrence et al., 1993; Kolpin et al., 1996; Kolpin et al., 1998; Kolpin et al., 2000a; Kolpin et al., 2000b). In the UK the number of field studies has been limited (Clark et al., 1991; Gooddy et al., 2001; Johnson et al., 2001; Gooddy et al., 2002a) with researchers often concentrating on laboratory studies of transport and degradation potential (Johnson et al., 1998; Besien et al., 2000; Johnson et al., 2000).

The major aquifer in the UK, the Cretaceous Chalk, is a soft microporous and fractured calcium carbonate commonly overlain by thin (<1 metre) calcareous soils. It is a complex natural system and consequently is very difficult to measure or sample in a systematic manner. Once a pesticide enters the chalk rock, the potential for biodegradation is substantially reduced (Johnson et al., 2000). With effect from December 2003, the European Union Drinking Water Directive (Council Directive 98/83/EC) has set limits of 0.03 µg/L for certain pesticides. Under the Directive there is currently no requirement for water supply organisations to measure pesticide metabolites despite evidence that their toxicity can be higher than the parent compound (Tixier et al., 2000; Tixier et al., 2001). There is a clear need to understand the movement and transport of pesticides and their degradation products in both the thin soil zone, where most retardation and degradation is likely to take place, and in the aquifer itself. In this study we have applied diuron and bromide (a conservative tracer) in successive years to a trial site. We have made a series of laboratory measurements based on field samples to determine the concentration of diuron and its metabolites under normal herbicide application rates and environmental conditions.

Diuron (*N*'-[3,4-dichlorophenyl]-*N,N*-dimethylurea) is a substituted urea herbicide used to control a wide variety of annual and perennial broadleaf and grassy weeds. It is used on many agricultural crops such as fruit, cotton, sugar cane, alfalfa, and wheat but is more widely applied for long-term pre-emergence weed control in non-crop areas (Tomlin, 1994) especially along railway lines (Schweinsberg et al., 1999). It may be found in formulations as wettable powders and suspension concentrates. Diuron works by inhibiting photosynthesis. It is relatively persistent in soil, with half-lives from 1 month to 1 year (Wauchope et al., 1992). Its persistence in soil is due to a combination of three properties: chemical stability, low water solubility and strong adsorption to soil particles (Walker and Jurado-Exposito, 1998). Microbial degradation is considered to be the primary mechanism for its dissipation from soil (Tixier et al., 2000).

This report details the findings from the second year of an on-going project into the fate of herbicides and their metabolites in the unsaturated zone of UK aquifers. The main aim of the project in the second year was to see if enhanced rates of degradation occurred in the field following reapplication of a pesticide in successive years. Several studies have investigated this phenomena for diuron in the field (Ronchaud et al., 2000; Tworkoski et al., 2000;) and the laboratory (Cox et al., 1996; Cullington and Walker, 1999) with some enhanced degradation of the parent observed. However, only few studies have measured degradation products (Cox et al., 1996; Gooddy et al., 2002a) and only one made the distinction between solid and liquid phases (Gooddy et al., 2002a).

2 Methods

2.1 FIELD SITE AND SAMPLING

The field site is situated near Wallingford, UK (NGR 46141898, 1°06' W 51°36' N). The site lies 250 m west of the topographical gradient change indicating the edge of the outcrop of the Lower Chalk and is situated over 1st (Flood Plain) Terrace deposits of Younger River Gravels in the valley of the River Thames (Avery, 1980). The soil is roughly 50 cm thick and is typical of brown calcareous earths of the Coombe 2 series, although near to the boundary of the argillic brown earths of the Sutton 2 series. Below 50 cm, a thin band of chalky material is encountered but no River Gravels were excavated as auguring was ceased at 54 cm.

To investigate the in situ degradation of diuron we devised a small experimental plot. The plot comprises a 3 x 3 m grid with a small, 5 m deep observation borehole constructed towards its northern end. On the 9th January 2001 at 11.30 am, a solution containing 6.03 g of an agricultural grade of a commercially available form of diuron, Karmex® (Du Pont chemicals), and 180 g of KBr in 9 litres of Wallingford tap water (approximately pH 7) was prepared in a clean 10 L watering can and applied to the plot by hand. The concentration of diuron applied is equivalent to 6.7 kg/ha which is the maximum recommended application rate. The findings of the study from year 1 are detailed in Gooddy et al. (2002b).

On 28th January 2002 at 11.30 am, a solution 6.03 g of Karmex® was reapplied to the 3 x 3 m plot in a similar manner to the 2001 application. In addition, an adjacent 3 x 3 m plot was constructed and the same concentration of Karmex and KBr as used in the first year was also applied. The KBr application is equivalent to 200 kg/ha or 134 kg/ha of Br and was applied to act as a conservative tracer of the downward flux of water. This concentration is unlikely to have any influence on the natural microbiological community present in the soil zone.

Precipitation was measured by a local rainfall collector situated roughly 50 m from the experimental plot. Figure 2.1 shows the distribution of rainfall that occurred during the 115 days of the monitoring period and for one week either side. A total of 245 mm fell on the days when rainfall occurred. On 46 occasions daily rainfall exceeded 1 mm. No rain fell on the day of application. During the complete period of January-May 2002 a total of 245 mm fell in the area, this compares with a 20 year median for the site of 235 mm which suggests this part of the winter was marginally wetter than normal.

Soil profiles down to 54 cm were obtained with an Edelman (Dutch) auger. Samples were taken every 9 cm and profiles were taken in duplicate with equivalent depths mixed in a polythene bag. Samples from both experimental plots were taken after 1, 15, 29, 42, 52, 73, 94 and 115 days. After each profile had been taken the small hole that remained was covered with surrounding material and marked so that it was not resampled at a later date.

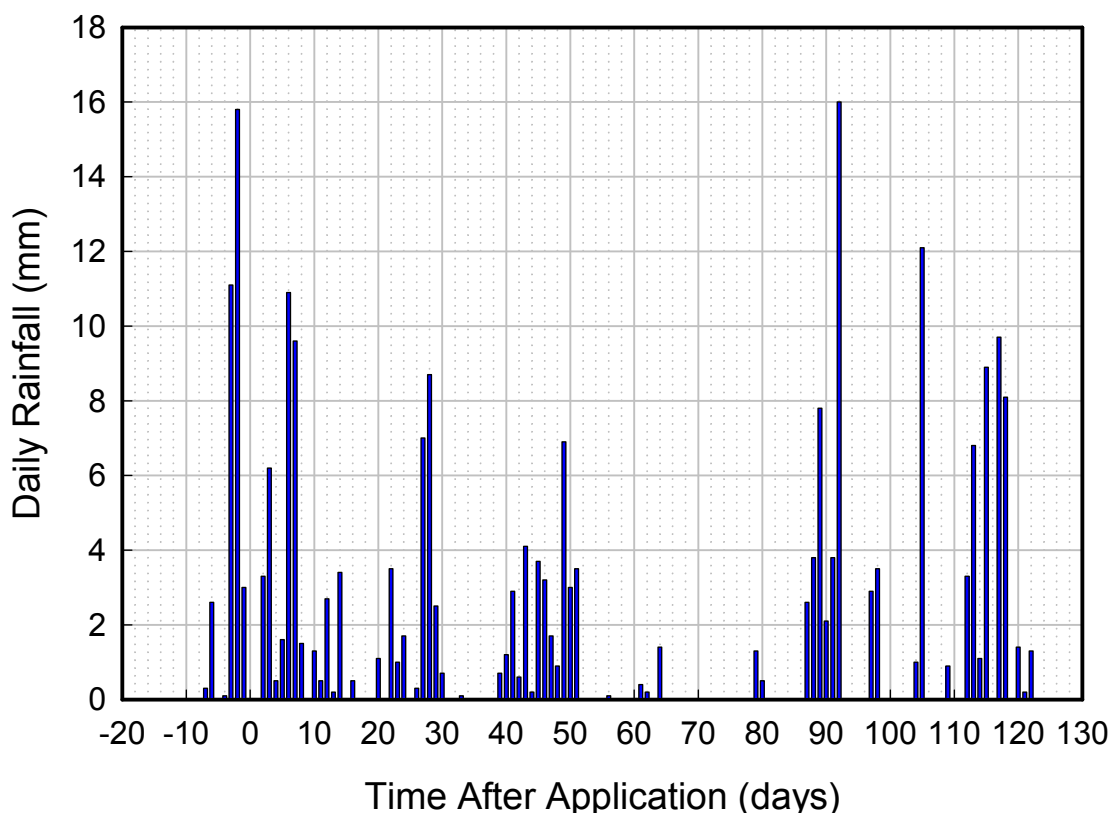


Figure 2-1 Bar chart showing rainfall at the site from January 21st 2002 to May 30th 2002.

In the laboratory approximately 300 g of soil from each of the samples were loaded into the buckets of a six arm JA 14 fixed angle rotor in a refrigerated Beckman J2-21 high speed centrifuge. Specially made Delrin liners with collection cups and pre-filters held the soil in the centrifuge rotor. The samples were centrifuged at 14,000 rpm (equivalent to a driving force of about 1.7 MPa) for 35 minutes at 4°C, and the pore water was extracted using the centrifuge drainage method (Edmunds and Bath, 1976). Great care was taken to avoid contamination and to minimize evaporation. Pore waters were extracted on the same day as soil sampling. The resultant porewaters were divided into 2 fractions: 2ml unfiltered and unacidified for bromide and a minimum of 10ml unfiltered and unacidified for diuron and metabolites. The centrifuged soil residues were preserved in a refrigerator at 4°C for 1 day prior to extraction by methanol and subsequent analysis for diuron and metabolites. These residues represent diuron and metabolites that are sorbed to the soil surface.

2.2 DIURON AND METABOLITE ANALYSIS

Initial HPLC method development was based on a previously published method (Field et al., 1997). The method involved the separation of diuron and its metabolites on a base-deactivated reversed-phase C18 Supelco LC18-DB column. However, in contrast to Field and coworkers, it was found that gradient elution was not necessary to provide good chromatography. Preliminary experiments using solutions of pure diuron and pure metabolites (QM_x Laboratories, Saffron Walden, UK), in conjunction with various isocratic compositions of a simple binary mobile phase consisting of acetonitrile and water, resulted in the formulation of an optimum mobile phase composition of 35% acetonitrile : 65% water. Chromatograms produced with this gave retention times of *ca.* 8 mins. for DCPU, *ca.* 11 mins. for DCPMU, *ca.* 14 mins for diuron and *ca.* 20 mins. for DCA. Detection was conducted with a sensitive UV/Vis detector (Waters 2487) set at 252 nm. By using a large sample introduction loop of 1 ml capacity a detection limit in the region of 50 ng/L was achieved. Good detection limits on small volumes of sample is crucial to this study due to the serious time penalty of centrifuging large masses of soil to obtain enough

water for a pre-concentration step. Small sample size also meant that many samples could be taken from the study plot without causing the serious disruption to the site that shallow coring using a drilling rig would cause.

A 2 mg/L aqueous solution of the commercial agrochemical form of diuron (Karmex) was prepared and analysed by HPLC. The chromatograms obtained indicated that the formulation contained 84% weight for weight (w/w) diuron (compared with 80% stated by the manufacturer) together with 0.1% w/w DCPMU, 0.1% w/w DCA and 0.01% w/w DCPU.

Porewater was analysed directly by injection of 1 ml onto the HPLC system. On completion of an HPLC analysis the column was backflushed with 80% aqueous acetonitrile to remove any strongly retained materials that might otherwise elute on later runs with possibly deleterious effects on peak quantification.

For the soil samples, roughly 200 g of a given post-centrifuged soil was transferred into a conical beaker and accurately weighed. To this was added twice as much methanol by weight. The mixture was carefully stirred with a large palette-knife type spatula which was also used to breakdown large soil aggregates. The beakers and their contents were then placed in a heated ultrasonic bath (40°C) and sonicated at intervals over a 24 h period. Further stirring with the spatula was performed intermittently over a 24 h period. The contents of each beaker were then transferred to a Buchner funnel and filtered through Whatman No. 41 filter paper. The residue was rinsed with methanol and the filtrate was reduced in volume on a rotary evaporator until the methanol had been removed. The resulting mainly aqueous suspension was made to an appropriate volume with pure water, sonicated and a 1 ml volume injected through the HPLC system. Again a post-run backflushing regime was employed to preserve the column and avoid quantification artefacts.

3 Results

3.1 SOIL MOISTURE CONTENT AND YIELD

Soil moisture contents were measured on each sampling occasion and have been presented graphically in Figure 3.1

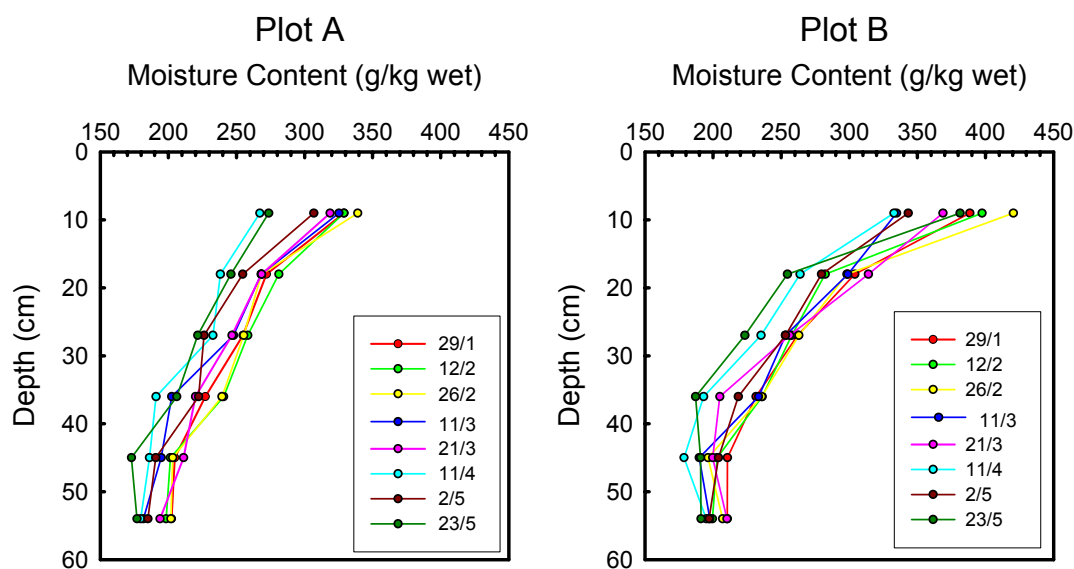


Figure 3-1 Variation with in moisture content with depth and time for plots A and B.

As demonstrated by Figure 3.1, the top of the profile for Plot B has a considerably higher moisture content than Plot A. A reduction in moisture content of about 50% and 100% from the top to the bottom of the profile can be observed for Plots A and Plots B respectively. The statistical analysis however shows that this difference is damped over the profile with the mean moisture content only indicating a 7% difference and the median showing a 2% difference. The bottom half of the profile at Plot A has a higher moisture content than the bottom half of the profile at Plot B.

It is interesting to note that the yields from Plot B are on average roughly 1/3rd higher than Plot A which reflects differences in soil drainage characteristics and likely explains the different moisture profiles.

Table 3-1 Simple statistical summary of soil moisture content and percentage yield for the two experimental plots

	Plot A		Plot B	
	Moisture (wet) g/kg	Yield (%)	Moisture (wet) g/kg	Yield (%)
Maximum	339	33	524	39
Minimum	173	6	187	8
Mean	237	14	254	19
Median	230	14	235	17

3.2 DIURON IN POREWATERS

The maximum detected concentrations of diuron and metabolites are given in Table 3.2. The maximum concentration of diuron in Plots A and B was observed at the top of the profile. In Plot B this maximum was detected 1 day after application, however, the maximum concentration of diuron in Plot A was observed 29 days after application. The maximum concentration of DCPMU was observed after 95 days in both plots, similarly the maximum concentration of DCPU was observed in both plots after 29 days. The highest concentration of DCA was found in Plot A after 115 days and in Plot B after 73 days..

Table 3-2 Maximum concentrations of diuron and its metabolites observed in porewaters taken from the two plots between January and May 2002.

	Diuron µg/L	DCPMU µg/L	DCPU µg/L	DCA µg/L
Plot A	373	48	7.8	3.1
Plot B	1450	63	20	1.0

The percentage number of samples with porewater concentrations greater than 0.1 µg/L and 1 µg/L is given in Table 3.3. Over the 115 day sampling interval, all samples contained more than 1 µg/L diuron. Despite the generally higher maximum concentrations of diuron and metabolites found in Plot B, more samples from Plot A exceed 1 µg/L and 0.1 µg/L when considering both the parent compound and its metabolites.

Table 3-3 Percentage of samples with diuron and metabolite porewater concentrations above 1 µg/L and 0.1 µg/L. Based on 48 samples.

	Diuron	DCPMU	DCPU	DCA
Plot A % > 1 µg/L	100	46	17	15
Plot B % > 1 µg/L	100	48	17	0
Plot A % > 0.1 µg/L	100	100	94	79
Plot B % > 0.1 µg/L	100	94	88	48

3.3 MASS BALANCE AND BROMIDE MOVEMENT

In order to assess the efficacy of the method and indeed the degree of sample heterogeneity, a mass balance has been performed based on the sum of diuron and metabolites in the both the porewaters and in the solid phase over the depth of the profile. Table 3.4 shows the enormous variance that occurs between the two plots and between sampling episodes. However, on average, nearly 100% of the diuron that has been applied can be accounted for in terms of the mass of diuron and metabolites.

Table 3-4 Percentage of applied diuron and metabolites recovered (solid and liquid phases combined) on each sampling occasion. Percentage of applied bromide recovered from porewaters in Plot B is also shown.

Sampling Date	% Application Plot A	% Application Plot B	% Application Plot B Bromide
29/01/2002	115	132	196
12/02/2002	113	21.2	170
26/02/2002	159	140	74.5
11/03/2002	79.3	120	129
21/03/2002	117	159	85.6
11/04/2002	41.8	67.1	262
02/05/2002	130	89.5	69.0
23/05/2002	38.2	48.6	43.2
Mean	99.0	97.2	129

Data for the mass of bromide recovered from the porewaters relative to the initial application of bromide is given in column four of Table 3.4. A high degree of variance is observed that does not follow the same pattern as the mass balance for the herbicide application to Plot B.

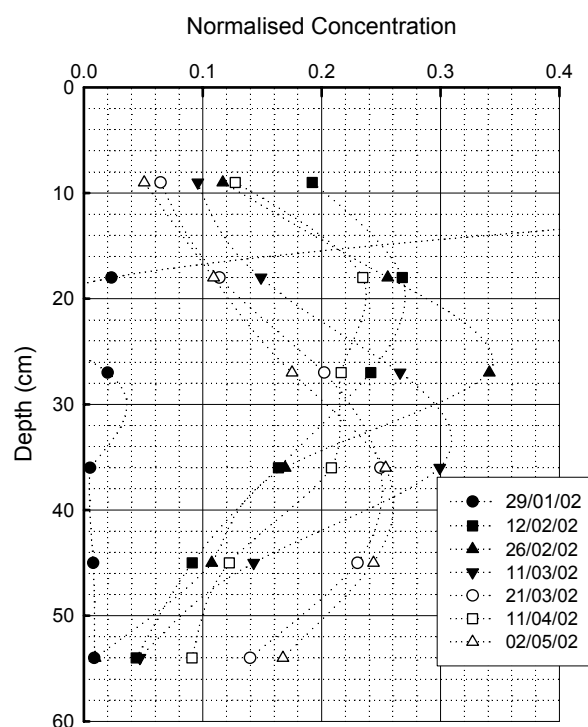


Figure 3-2 Bromide concentration with depth on each sampling occasion. Data has been normalised to maximum concentration found on each sampling occasion.

The movement of Br through the profile is shown in Figure 3.2. Due to the significant variation in Br recovered relative to the amount applied, the data has been normalised to the maximum concentration observed in the profile on a given sampling occasion. The plot shows the movement of a peak down through the profile which has reached *ca.* 18 cm after 15 days, *ca.* 27 cm after 29 days, *ca.* 33 cm after 42 days and *ca.* 40 cm after 115 days, although no more movement of the bromide peak is apparent after 52 days. Based on the first 52 days of the experiment, the Br moves at a rate of roughly 0.8 cm per day ($R^2 = 0.95$) as shown in Figure 3.3.

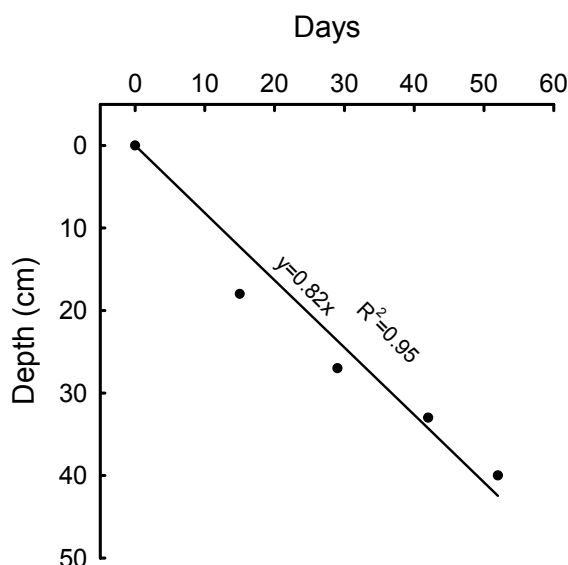


Figure 3-3 Peak bromide concentration as a function of depth and time.

3.4 TEMPORAL CHANGES IN DIURON AND METABOLITES

3.4.1 Porewaters

The reduction in the relative amount of diuron and increase in the relative amount of DCPMU in the soil solutions at the two plots is shown in Figure 3.4. Over the first 52 days, diuron is removed at a rate of 0.40% and 0.41% per day at Plot A and B respectively, which is roughly twice the rate recorded for Plot A in year 1 (Goody et al., 2002b) where the rate of disappearance was 0.21% per day. Over 115 days the rate of removal reduces to 0.29 % per day for Plot A but increases marginally to 0.44% per day for Plot B.

The rate of formation of DCPMU over the first 52 days occurs at a rate of 0.30% and 0.29% per day for Plots A and B respectively, which compares with a rate of formation of 0.18% per days for Plot A in year 1. Over 155 days, the rate of formation of DCPMU falls to 0.19% per day for Plot A but increases to 0.37% per day for Plot B.

Figure 3.5 shows how the porewaters are comprised in terms of the parent compound and all the degradation products. Relatively greater amounts of DCPMU and DCPU are found in Plot B than Plot A although Plot A contains relatively more of the final degradation product, DCA.

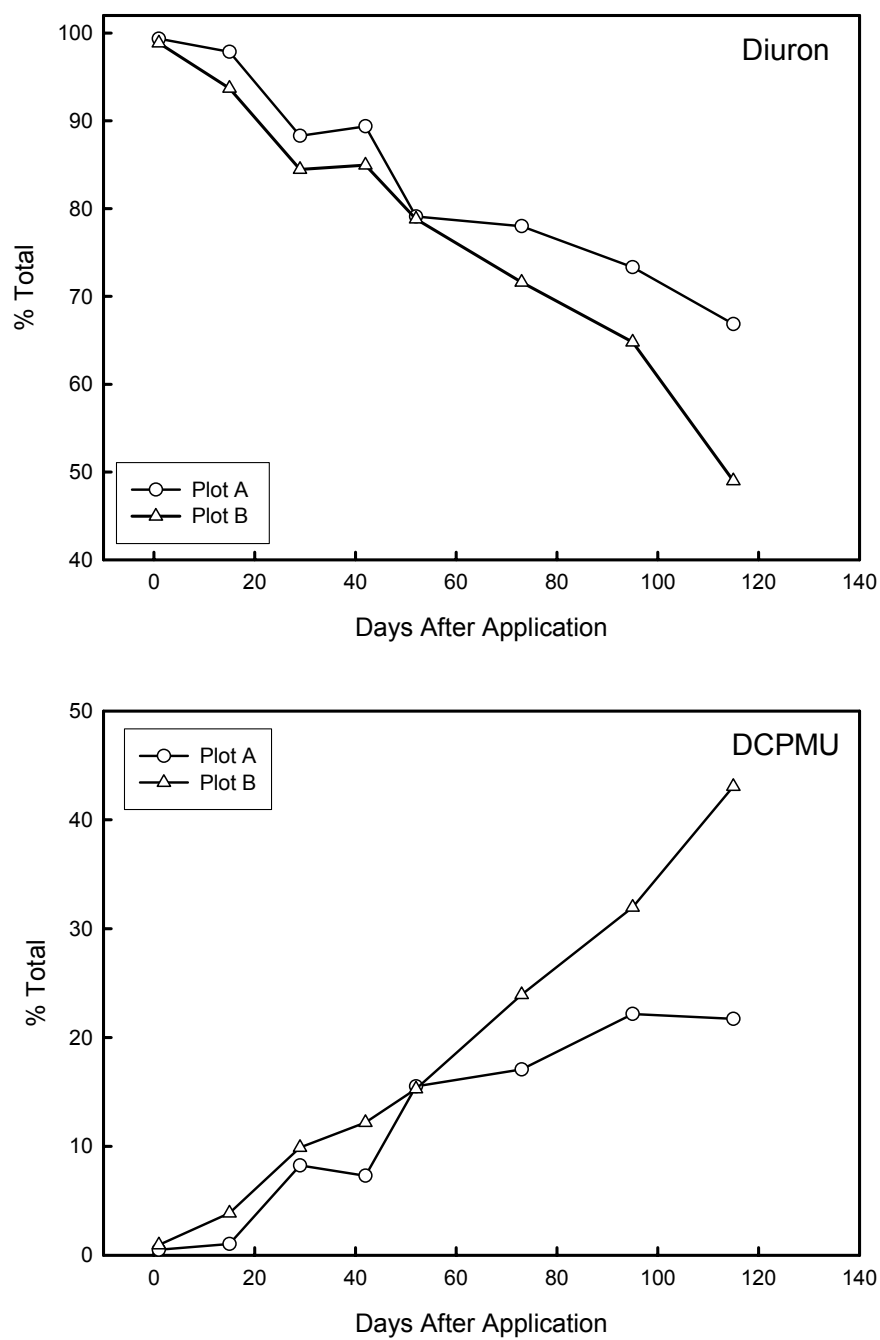


Figure 3-4 Relative amounts of diuron and the first degradation product, DCPMU, in the porewaters of Plot A and Plot B as a function of time after application.

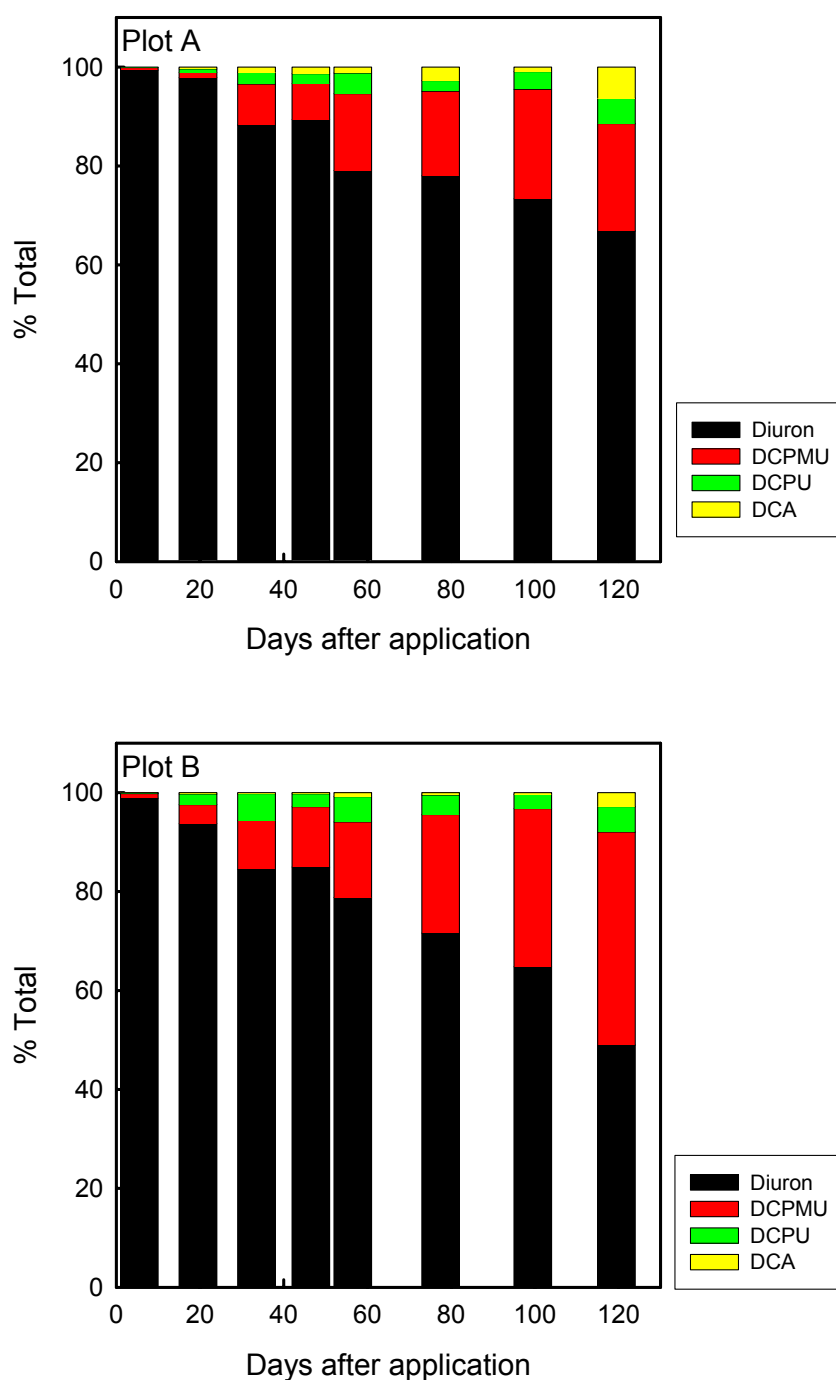


Figure 3-5 Bar chart showing the relative composition of porewaters for Plot A and Plot B as a function of time after application.

3.4.2 Solid Phase

The reduction in the relative amount of diuron and increase in the relative amount of DCPMU in the soil at the two plots is shown in Figure 3.6. Over the first 52 days, diuron is removed at a rate of 0.74% and 0.65% per day at Plot A and B respectively, which is roughly twice the rate recorded for Plot A in year 1 (Goody et al., 2002b) where the rate of disappearance was 0.39% per day. Over 115 days the rate of removal reduces to 0.46 % per day for Plot A decreases marginally to 0.62% per day for Plot B.

The rate of formation of DCPMU over the first 52 days occurs at a rate of 0.62% and 0.58% per day for Plots A and B respectively, which compares with a rate of formation of 0.34% per days

for Plot A in year 1. Over 155 days, the rate of formation of DCPMU falls to 0.40% per day for Plot A but increases to 0.53% per day for Plot B.

Figure 3.7 shows how the porewaters are comprised in terms of the parent compound and all the degradation products. Similarly to the porewaters, relatively greater amounts of DCPMU and DCPU are found in Plot B than Plot A although Plot A again contains relatively more of the final degradation product, DCA.

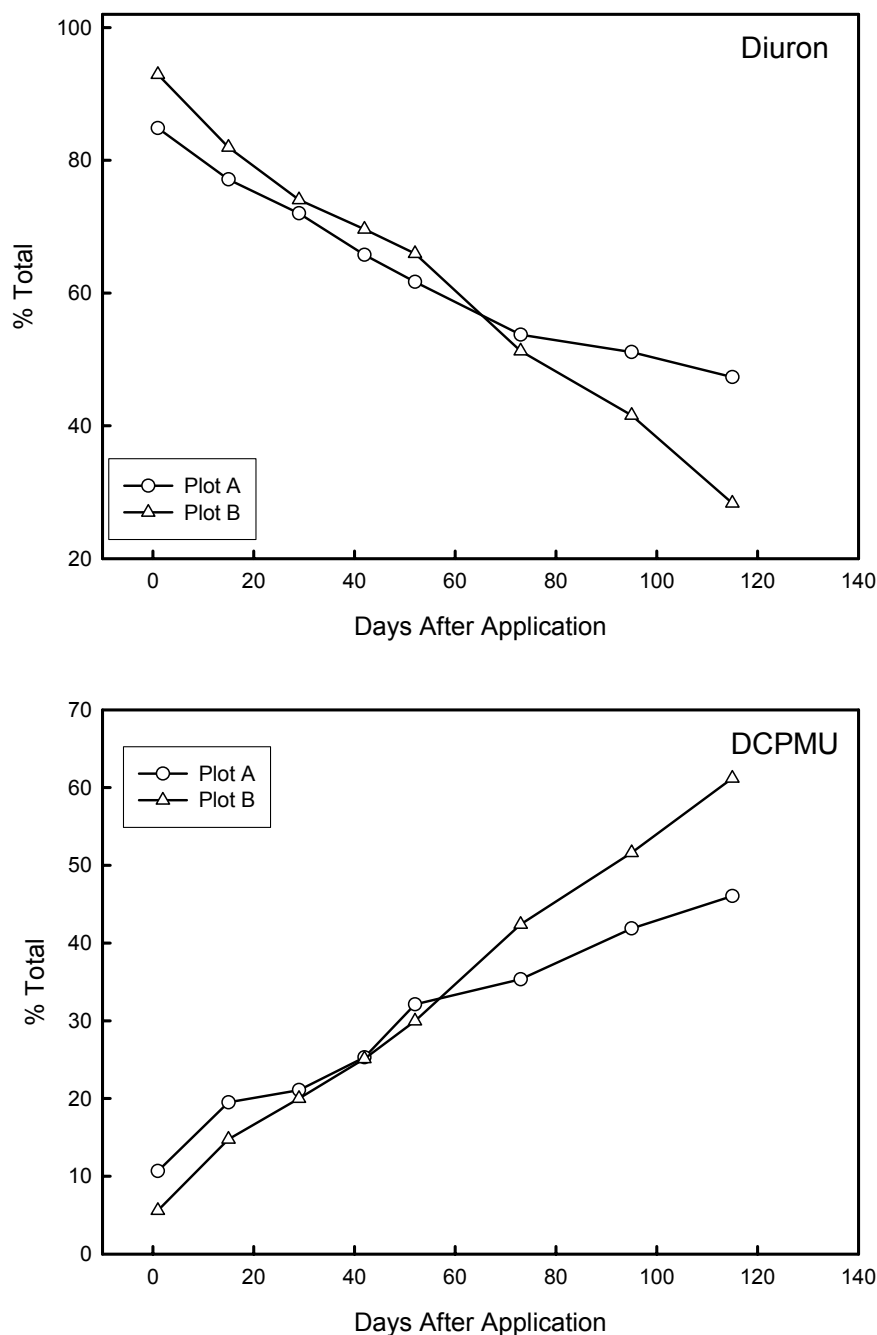


Figure 3-6 Relative amounts of diuron and the first degradation product, DCPMU, in the solid phase of Plot A and Plot B as a function of time after application.

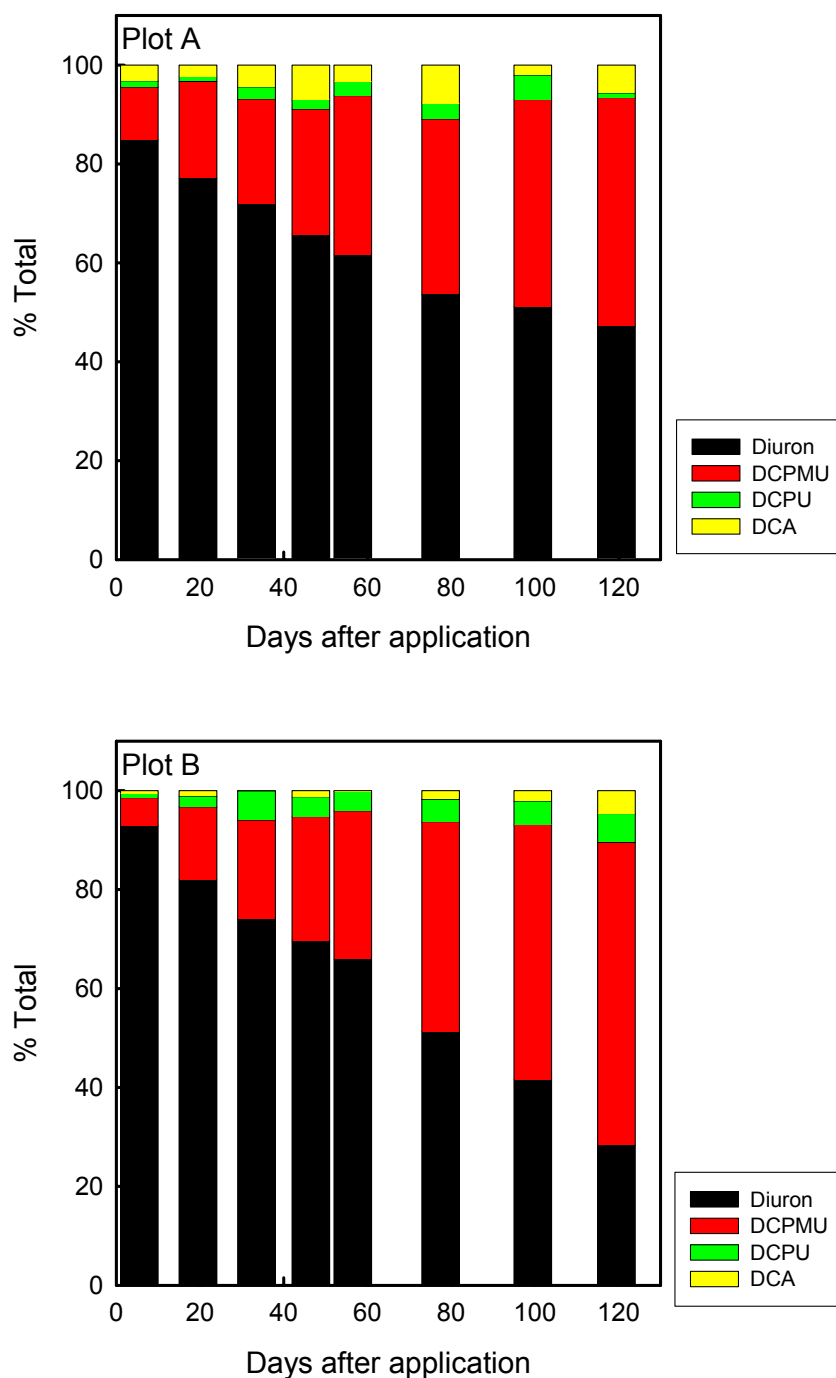


Figure 3-7 Bar chart showing the relative composition of solid phase for Plot A and Plot B as a function of time after application.

3.5 PARTITIONING BETWEEN SOLID AND LIQUID PHASES

The sorption and desorption of diuron from the soil solid phase has previously been noted as a potential sink and source of groundwater contamination (Reddy et al., 1992). A useful parameter for determining the preference of a compound for the solid or liquid phase is the partition

coefficient, K_d . The K_d is defined as:
$$K_d = \frac{\text{SolidPhaseConcentration}}{\text{LiquidPhaseConcentration}}$$

Where the solid phase concentration is measured in $\mu\text{g/kg}$ and the liquid phase is measured in $\mu\text{g/L}$. The units of the K_d are L/kg .

Figure 3.8 shows partition coefficients for diuron and DCPMU in Plots A and B. For both Plot A and Plot B a relatively linear trend is observed between diuron and DCPMU, with K_d s for DCPMU roughly 5 times higher than those for diuron.

Table 3.5 provides a statistical summary of partition coefficients for the parent compound and degradation products in both Plots. Reddy et al. (1992) found K_d s for diuron in the range 0.84-3.26 L/kg for a sandy soil. This data shows a range of 0.6-86 L/kg. The K_d s measured in Plot B are generally lower than those measured in Plot A. From the mean it is possible to see that K_d varies such that:

$$DCA > DCPMU > DCPU > Diuron$$

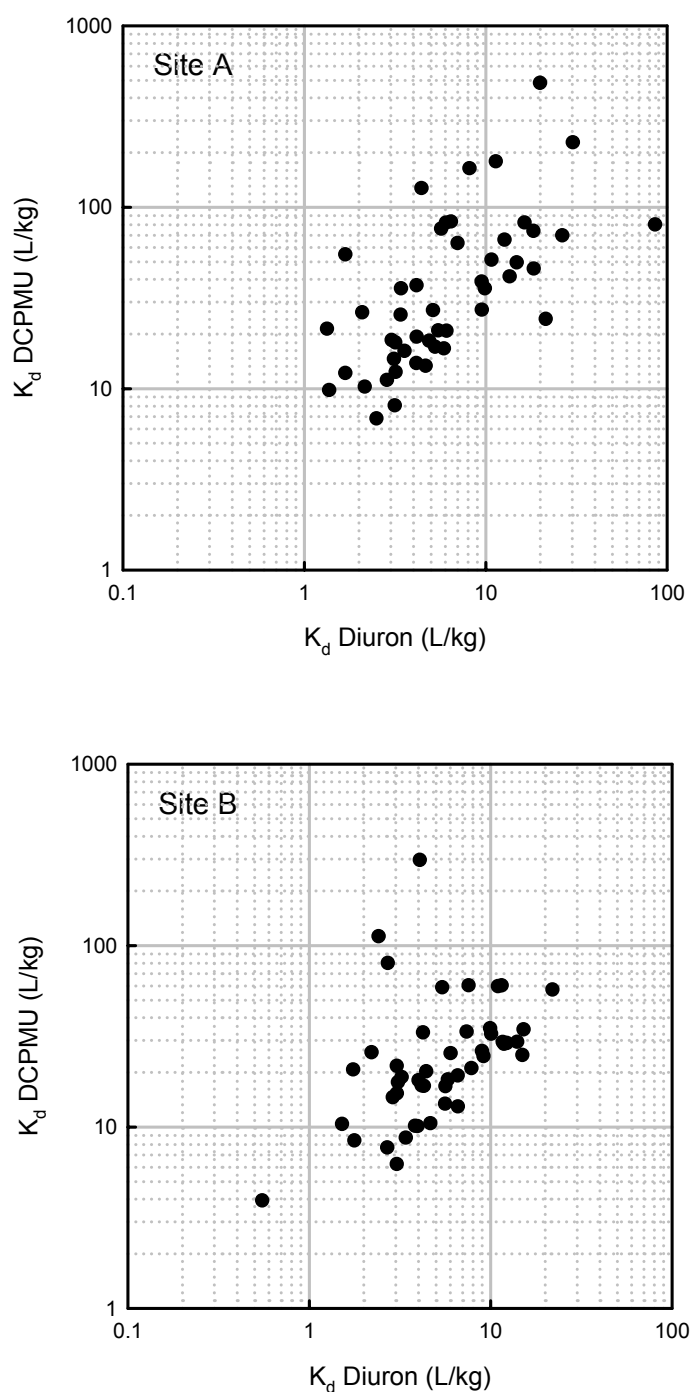


Figure 3-8 Cross plot of partition coefficients for diuron and DCPMU.

Table 3-5 Partition coefficients (L/kg) for diuron and metabolites in Plots A and B.

	Plot A				Plot B			
	Diuron	DCPMU	DCPU	DCA	Diuron	DCPMU	DCPU	DCA
Maximum	86	490	100	1100	22	300	66	510
Minimum	1.3	6.8	0.6	0.8	0.6	3.9	0.4	0.3
Mean	9.5	56	13	86	6.4	33	14	75
Median	5.4	27	3.4	29	4.6	21	7.8	17

4 Conclusions

Through carrying out a field experiment rather than laboratory column studies it has been possible to observe what happens to diuron and its metabolites under physical and chemical conditions typical of a soil overlying the Chalk. The development of a low volume, high sensitivity analytical method has enabled relatively cost effective, high resolution measurement of environmental processes. Despite the resolution used, it is still not possible to quantify the processes in detail due to the considerable degree of heterogeneity encountered. The extreme variability between the two plots and indeed between successive sampling is surprising. Figure 3.1 showed a very dramatic difference in the moisture contents of the adjacent plots which could have a significant impact on solute transport. The generally more moist Plot B containing generally higher concentrations of diuron and metabolites in the porewaters than Plot A (319 μg compared with 193 μg over the sampling period) and Plot A contains generally higher concentrations in the solid phase than Plot B (6600 μg compared with 6360 μg over the sampling period). A mass balance approach showed large variations in diuron distribution but on average accounted for 99% of the diuron applied to Plot A and 97% of the diuron applied to Plot B.

Bromide was not applied to Plot A in the winter of 2002 as it had previously been applied in 2001 and the residual porewater concentrations could make interpretation problematic. In light of the different moisture conditions observed in the two plots this is unfortunate and at least some information as to conservative solute transport might have been gleaned.

In year 2, the rate of degradation over a 50 day period is faster in both plots than it was in Plot A in year 1. After 120 days metabolites account for more than 50% of total pesticide found in solid phase in both plots (53% Plot A and 72% Plot B). In the liquid phase, metabolites account for 33% in Plot A and 51% in Plot B. The rate of degradation is faster in Plot B than Plot A for both solid phase and porewaters which is contrary to the original hypothesis under which the year 2 programme of work was undertaken. In all cases, the dominant metabolite is DCPMU. However, the highest percentage of DCA occurs in solid phase and porewaters of Plot A. This might suggest some enhanced degradation of DCPMU or could be a residual from the 2001 application.

Metabolites are more strongly retained in the solid phase than the parent compounds as demonstrated by the generally higher K_d values. Although greater rates of degradation are associated with the solid phase, this also suggests that metabolites can remain as a potential source of groundwater contamination long after the parent compound has disappeared from both porewaters and solid phase.

References

- AVERY, B W. 1980. Soil classification for England and Wales (higher categories). *Soil Survey Technical Monograph No. 14*.
- BAKER, D B, BUSHWAY, R J, ADAMS, S A, and MACOMBER, C. 1993. Immunoassay screens for alachlor in rural wells - false positives and an alachlor soil metabolite. *Environmental Science and Technology*, Vol 27, 562-564.
- BESIEN, T J, JOHNSON, A C, and WILLIAMS, R J. 2000. Isoproturon and bromide breakthrough curves from chalk cores in laboratory studies. *Journal of Contaminant Hydrology*, Vol 43, 91-110.
- CHILTON, P J, STUART, M E, LAWRENCE, A R, GOODDY, D C, WILLIAMS, R J, and JOHNSON, A C. 2000. Assessing pesticide pollution of groundwater: Current knowledge and remaining gaps. In O. Sililo et al. (eds) International Association of Hydrogeologists XXXth Congress – Groundwater: Past Achievements And Future Challenges, 26 November – 1 December 2000, Cape Town, South Africa, 17-25.
- CLARK, L, GOMME, J, and HENNINGS, S M. 1991. Study of pesticides in waters from a Chalk catchment, Cambridgeshire. *Pesticide Science*, Vol 32, 15-33.
- COX, L, WALKER, A, AND WELCH, S J. 1996. Evidence for accelerated degradation of isoproturon in soils. *Pesticide Science*, 48, 253-260.
- CULLINGTON, J E, AND WALKER, A. 1999. Rapid biodegradation of diuron and other phenylurea herbicides by a soil bacterium. *Soil Biology and Biochemistry*, Vol 31, 677-686.
- EDMUNDS, W M, and BATH, A H. 1976. Centrifuge extraction and chemical analysis of interstitial waters. *Environmental Science and Technology*, Vol 10, 467-472.
- FIELD, J A, REED, R L, SAWYER, T E, and MARTINEZ, M. 1997. Diuron and its metabolites in surface water and ground water by solid phase extraction and in-vial elution. *Journal of Agriculture and Food Chemistry*, Vol 45, 3897-3902.
- FOSTER, S S D, CHILTON, P J, and STUART, M E. 1991. Mechanisms of groundwater pollution by pesticides. *Journal of the Institute of Water and Environment Managers*, Vol 5, 186-193.
- FOSTER, S S D. 2000. Assessing and controlling the impacts of agriculture on groundwater – from barley barons to beef bans. *Quarterly Journal of Engineering Geology and Hydrogeology*, Vol 33, 263-280.
- GAUS, I. 2000. Effects of water extraction in a vulnerable aquifer: Consequences for groundwater contamination by pesticides, Sint-Jansteen area, The Netherlands. *Hydrogeology Journal*, Vol 8, 218-229.
- GOODDY, D C, BLOOMFIELD, J P, CHILTON, P J, JOHNSON, A C, and WILLIAMS, R J. 2001. Assessing herbicide concentrations in the saturated and unsaturated zone of a Chalk aquifer in Southern England. *Ground Water*, Vol 39, 262-271.
- GOODDY D C, CHILTON P J and HARRISON I. 2002a. A field study to assess the degradation and transport of diuron and its metabolites in a calcareous soil. *Science of the Total Environment* 297, 1-3, 67-83.
- GOODDY D C, HARRISON I, ALLEN D, CARLICK C and CHILTON P J. 2002b. A field study to assess the degradation and transport of diuron and its metabolites in calcareous sediments. British Geological Survey Internal Report IR/02/022.
- JOHNSON, A C, HUGHES, C D, WILLIAMS, R J, and CHILTON, P J. 1998. Potential for aerobic isoproturon biodegradation and sorption in the unsaturated and saturated zones of a chalk aquifer. *Journal of Contaminant Hydrology*, Vol 30, 281-297.
- JOHNSON, A C, WHITE, C, and BHARDWAJ, C L. 2000. Potential for Isoproturon, atrazine and mecoprop to be degraded within a chalk aquifer system. *Journal of Contaminant Hydrology*, Vol 44, 1-18.
- JOHNSON, A C, BESIEN, T J, BHARDWAJ, C L, DIXON, A, GOODDY, D C, HARRIS, A H, and WHITE, C. 2001. Penetration of herbicides to groundwater in an unconfined chalk aquifer following normal soil applications. *Journal of Contaminant Hydrology*, Vol 53, 101-117.
- KOLPIN, D W, THURMAN, E M, and GOOLSBY, D A. 1996. Occurrence of selected pesticides and their metabolites in near-surface aquifers of the Midwestern United States. *Environmental Science and Technology*, Vol 30, 335-340.
- KOLPIN, D W, BARBASH, J E, and GILLIOM, R J. 1998. Occurrence of pesticides in shallow groundwater of the United States: Initial results from the National Water-Quality Assessment Program. *Environmental Science and Technology*, Vol 32, 558-566.
- KOLPIN, D W, BARBASH, J E, and GILLIOM, R J. 2000a. Pesticides in ground water of the United States, 1992-1996. *Ground Water*, Vol 38, 858-863.
- KOLPIN, D W, THURMAN, E M, and LINHART, S M. 2000b. Finding minimal herbicide concentrations in ground water? Try looking for their degradates. *Science of the Total Environment*, Vol 248, 115-122.
- LAWRENCE J R, ELDAN, M, and SONZOGNI, W C. 1993. Metribuzin and metabolites in Wisconsin (USA) well water. *Water Research*, Vol 27, 1263-1268.
- REDDY, K N, SINGH, M and ALVA, A K. 1992. Sorption and desorption of diuron and norflurazon in Florida citrus soils. *Water, Air and Soil Pollution*, Vol 64, 487-494.

- ROUCHRAD, J, NEUS, O, BULCKE, R, COOLS, K, EELEN, H, DEKKERS, T. 2000. Soil dissipation of diuron, chlorotoluron, simazine, propyzamide, and diflufenican herbicides after repeated applications in fruit tree orchards. *Archives of Environmental Contamination and Toxicology*, Vol 39, 60-65.
- SCHWEINSBERG, F, ABKE, W, RIETH, K, ROHMANN, U, and ZULLEI-SEIBERT, N. 1999. Herbicide use on railway tracks for safety reasons in Germany? *Toxicology Letters*, Vol 107, 201-205.
- SOUTTER, M, and PANNATIER, Y. 1996. Groundwater vulnerability to pesticide contamination on a regional scale. *Journal of Environmental Quality*, Vol 25, 439-444.
- THURMAN, E M, GOOLSBY, D A, MEYER, M T, MILLS, M S, POMES, M L, and KOLPIN, D W. 1992. A reconnaissance study of herbicides and their metabolites in surface-water of the Midwestern United States using immunoassay and gas-chromatography mass-spectrometry. *Environmental Science and Technology*, Vol 26, 2440-2447.
- TIXIER, C, SANCELME, M, BONNMOY, F, CUER, A, and VESCHAMBRE, H. 2001. Degradation products of a phenylurea herbicide diuron: Synthesis, ecotoxicity, and biotransformation. *Environmental Toxicology and Chemistry*, Vol 20, 1381-1389.
- TIXIER, C, BOGAERTS, P, SANCELME, M, BONNMOY, F, LANDOALD, T, CUER, A, BOHATJET, J, and VESCHAMBRE, H. 2000. Fungal biodegradation of a phenylurea herbicide, diuron: Structure and toxicity of metabolites. *Pesticide Management Science*, Vol 56, 455-462.
- TOMLIN, C D S. 1994. The Pesticide Manual, A World Compendium, In: Tomlin CDS (Ed.), Incorporating the Agrochemicals Handbook. Tenth edition. Published jointly by the British Crop Protection Council (Farnham, UK) and the Royal Society of Chemistry (Cambridge, UK).
- TWORKOSKI, T J, WELKER, W V, and VASS, G D. 2000. Soil residues following repeat applications of diuron, simazine and Terbacil. *Weed Technology*, Vol 14, 191-196.
- WALKER, A, and JURADO-EXPOSITO, M. 1998. Adsorption of isoproturon, diuron and metsulfuron-methyl in two soils at high soil:solution ratios. *Weed Research*, Vol 38, 229-238.
- WAUCHOPE, R D, BUTTLER, T M, HORNSBY, A G, AUGUSTIJN-BECKERS, P W M, and BURT, J P. 1992. SCS/ARS/CES Pesticide properties database for environmental decision making. *Reviews in Environmental Contamination and Toxicology*, Vol 123, 1-157.